PROCEEDINGS OF

THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

The Relation between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution.— Part III.

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(Communicated by Sir James Dewar, F.R.S. Received July 29,—Read December 11, 1913.)

Theoretical Part.

The investigation of the crystalline properties of the simpler organic bodies, gaseous or liquid at ordinary temperature, has been described in Parts I and II.* In this paper the experimental results will be discussed with regard to their bearing upon the problem of the relationship between molecular constitution and crystal symmetry.

In order to facilitate a comparison the experimental results are summarised in the table on p. 2.

As seen from the table, more than 50 per cent. of the substances investigated are polymorphic, and to this class nearly all the substances which contain only one carbon atom belong. The question therefore arises which one of the crystalline modifications of a substance is to be compared with the one or the other form of another substance, or with the crystals of a substance of which only one modification is known. In most of the cases investigated very little is known with regard to the modification stable at low temperature, and thus for practical reasons only the form crystallising directly out of the liquid state can be taken into account. Also, from

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 354 (1913); and vol. 89, p. 327 (1913).

Substance.	Crystal-form on crystallisation from the liquid state.	Polymorphism.
CH_4	Cubic	Dimorphic *e**
CH_3Cl	Orthorhombic or monoclinic	—
CH_2Cl_2	Orthorhombic	Dimorphic *e*
$CHCl_3$	Hexagonal†	—
CCl_4	Cubic	Dimorphic *e*
CH_3Br	Monoclinic	Trimorphic *e*
CH_2Br_2	Orthorhombic	Dimorphic *e*
$CHBr_3$	Hexagonal	Dimorphic *e*
CBr_4	Cubic	Dimorphic *e*
CH_3I	Monoclinic	—
CH_2I_2	Orthorhombic	Tetramorphic *e*‡
CHI_3	Hexagonal	(Dimorphic ?)
CI_4	Cubic	—
$CH_3(NO_2)$	Monoclinic	—
$C(NO_2)_4$	Cubic	Dimorphic *e*
$CCl_3(NO_2)$	Tetragonal, hexagonal, or orthorhombic	Dimorphic *e*
CO	Cubic	—
CO_2	"	—
CS_2	Monoclinic or triclinic	—
COS	Tetragonal, hexagonal, or orthorhombic	—
$COCl_2$	Tetragonal or hexagonal	Dimorphic *m*
$CH_3.CH_3$	Hexagonal	—
$CH_2:CH_2$	Monoclinic	—
$CH\vdots CH$	Cubic	Dimorphic *e*
$CH_3.CH_2.CH_3$	Orthorhombic or monoclinic	Dimorphic *e*
$CH(CH_3)_3$	Hexagonal	—
$CH_3.CH_2.CH_2.CH_3$	"	Dimorphic *e*
$CH_3.(CH_2)_3.CH_3$	Orthorhombic or monoclinic	—
$CH_3.(CH_2)_4.CH_3$	Monoclinic or triclinic	—
$CH_3.(CH_2)_5.CH_3$	" "	—
$CH_3.(CH_2)_6.CH_3$	" "	—
$C(CH_3)_4$	Cubic	Dimorphic *e*
$CH_3.OH$	Monoclinic or triclinic	Dimorphic *e*
$C_2H_5.OH$	Orthorhombic, monoclinic, or triclinic	—
$C(CH_3)_3.OH$	Hexagonal	Dimorphic *e*
$CH_3.O.CH_3$	Orthorhombic	—
$CH_3.O.C_2H_5$	Monoclinic or triclinic	—
$C_2H_5.O.C_2H_5$	Orthorhombic	Dimorphic *m*
$CH_3.CO.CH_3$	Monoclinic or triclinic	—
$C(O.CH_2.CH_3)_4$	Tetragonal (pseudocubic)	—
$C(CH_2.OH)_4$	Tetragonal	—
$\underline{CH_2.CH_2.CH_2}$	Hexagonal	—
$\underline{CH_2.CH_2.CH_2.CH_2.CH_2.CH_2}$	Cubic	Dimorphic *e*
$\underline{CH_2.CH_2.CH_2.CH_2.CH_2.CH}.CH_3$	Monoclinic	—
C_6H_6	Orthorhombic	—
$C_6H_5.CH_3$	"	—
1.4-$C_6H_4.(CH_3)_2$	Monoclinic	—
1.3.5-$C_6H_3(CH_3)_3$	Orthorhombic	Dimorphic *m*
$C_6(CH_3)_6$	"	—
C_6Cl_6	"	—
$C(C_6H_5)_4$	"	—

* *e* = enantiotropic ; *m* = monotropic.

† Hexagonal includes trigonal.

‡ According to Tammann and Hollmann.

a theoretical point of view, it seems that, in a comparison between the molecular structure and crystal form of a body, the modification which crystallises directly out of the liquid state or, in cases of monotropy, the modification of higher melting point, which is the stable form, should in the first place be taken into account, as it seems probable that the crystalline modification in equilibrium with the liquid at the melting point corresponds to the molecules predominant in the liquid and gaseous states.

In most cases where the complete crystallographic investigation of a substance is given in the literature the crystals investigated have been obtained by crystallisation from solution, either at room temperature or at a temperature only slightly higher. The crystals investigated are therefore often not those which are obtained directly from the liquid state, but correspond to another crystalline modification. An instance of considerable importance may serve to illustrate this. Carbon tetrabromide is given in Groth's handbook as being monoclinic, since the crystals obtained at room temperature from solutions are monoclinic. On heating, these crystals change into a regular form at $+46°$, and the regular form melts at ordinary pressures at $92{\cdot}5°$. Therefore in the table given here carbon tetrabromide is mentioned as regular, but dimorphic. Cases like this are numerous, and, in order to enable comparisons to be made, all substances which are quoted in this paper have been investigated optically at a temperature immediately below the melting point, with a view to ascertaining whether the modification described in the literature is the one formed directly out of the liquid condition, or whether it is another polymorphic modification.

In the first series of results published on the investigations of bodies gaseous or liquid at ordinary temperatures, it has been briefly pointed out with regard to the optical method of determining the crystal system of a body that it is, of course, not in all cases possible to determine by such a method to what crystal system a body belongs, as the crystals of some substances incline to grow only in certain crystallographic directions. It will be noticed from the summary of the experimental results that it has, as a matter of fact, not been possible to determine in some instances to which crystal system a body does belong, but that two or three alternatives are given. It seems, therefore, fitting at this stage to point out that the crystal-optical method, although it gives results which in most cases render the exact determination of the crystal system of a body possible, and also gives valuable information about the general properties in the solid state of substances gaseous or liquid at ordinary temperature, is not intended to replace an ordinary crystallographic investigation, but to be used in cases which hitherto have been entirely inaccessible to crystallographic research, although from the point of view of general chemistry they are of great importance. The experimental results of this investigation and the theoretical conclusions drawn from them have to be judged from this point of view.

Discussion of Results.

(a) *Compounds containing One Carbon Atom.*—In order to facilitate discussion the compounds containing one carbon atom will be dealt with first, and the substances containing several carbon atoms will then be considered. In view of the tetravalency of carbon, methane may be regarded as the parent substance from which all the other carbon compounds may be derived by substitution of the hydrogen atoms. The tetra-substitution products of methane, in which all the substituents are equal among themselves, may further be regarded as being equivalent with methane from the point of view of the architecture of the molecule. The question therefore at once arises whether to this highest degree of symmetry of the chemical molecule there corresponds a crystal form of high symmetry, irrespective of the nature of the atoms attached to the carbon atom, or whether the character of the four atoms attached to the carbon atom determines the crystal form of the compound. This is, of course, only a special instance of the general question whether the crystal form is an "additive" property depending on the specific properties of each constituent which makes up the compound, or whether the crystal form is a "constitutive" property, depending not on the specific properties of the constituents but on the constitution of the compound.

Carbon itself is known in two crystalline modifications, diamond and graphite, the one regular, the other hexagonal. In the carbon tetra-compounds, methane, carbon tetrachloride, carbon tetrabromide, carbon tetra-iodide, tetranitro-methane, and tetramethyl-methane, the carbon atom is associated with hydrogen, which in the elementary state crystallises in the regular crystal system,* with chlorine which is orthorhombic,† with bromine which is orthorhombic,‡ with iodine which is orthorhombic, but which has besides been observed to occur in a monoclinic modification, and lastly with the $—NO_2$ and $—CH_3$ groups, of the eventual specific crystalline properties of which nothing can be said. All these compounds have been proved to crystallise as regular crystals out of the liquid state. If the specific crystallographic properties of the atoms as they appear in the elementary state—

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 64 (1913).

† 'Roy. Soc. Proc.,' A, vol. 88, p. 350 (1913).

‡ 'Roy. Soc. Proc.,' A, vol. 88, p. 352 (1913).

or, more correctly, the forces which act to make an element crystallise in a certain manner—would also determine the crystal system of the compounds of this element, we should expect that out of the above compounds only methane would be regular, but that on the other hand carbon tetrachloride, as being built up out of one atom which in the elementary state is regular, and four atoms which in the elementary state are orthorhombic, would show a less degree of symmetry and be rhombic or possibly tetragonal. From the fact here established that all these compounds crystallise in the regular crystal system, the conclusion must be drawn, that the specific crystal form of an element does not determine the crystal form of its compounds, that is that:

The crystal form is not an additive property of matter.

The same conclusion may also be drawn from the circumstances that the oxides of carbon and several other oxides are regular, although oxygen, as has recently been found,* does not crystallise in the regular crystal system.

The above does not imply that the properties of the atoms themselves as manifested in their crystalline form in the elementary state, or the forces which cause them to crystallise in a certain form in the elementary state, have no influence at all upon the crystal angles or the crystal form of the compounds. On the contrary, it seems almost certain that this is to some extent the case, at least in a secondary way.

We may proceed to discuss the mono-, di-, and tri-substitution products, in which the substituents are identical among themselves, on the assumption that the crystal form is a constitutive property. The mono-substitution products CH_3Br, CH_3I, CH_3NO_2, have been found to be monoclinic, CH_3Cl rhombic or monoclinic, and $CH_3.OH$ monoclinic or triclinic. The di-substitution products CH_2Cl_2, CH_2Br_2, CH_2I_2, have been found to be orthorhombic; the tri-substitution products $CHCl_3$, $CHBr_3$, CHI_3, hexagonal. Di- and trinitro-methane have on account of their instability not been investigated. No other di- and tri-substitution products of methane which do not contain larger groups than the methane nucleus itself are available for comparison.

We thus observe that when one hydrogen atom in the regularly crystallising methane is substituted by some other univalent atom or group, the resulting compound crystallises in one of the crystal systems of comparatively low symmetry. By such a substitution the symmetrically built molecule of methane, consisting of one carbon atom with four hydrogen atoms grouped around it, is changed into a highly unsymmetrical molecule in which the carbon atom is surrounded in three directions of space by three hydrogen atoms and in the fourth by a much larger atom or group. If, then, one more hydrogen atom is substituted by an atom or group identical with the first substituent, the contrast in the molecule produced by the introduction of the first substituent becomes diminished, the molecule in this case consisting of a carbon atom surrounded by two pairs of atoms identical between themselves. As a result the crystal form of these di-substitution products shows a higher degree of symmetry, being orthorhombic, than that of the, mostly monoclinic, mono-substitution products. By introducing a third substituent, the symmetry of the molecule is further increased, as it now consists of the central carbon atom surrounded by three large atoms, which are identical between themselves, and the remaining hydrogen atom. The predominance of the three substituents manifests itself in the hexagonal crystal form of these bodies. If then the last hydrogen atom is similarly substituted, we obtain the tetra-substitution product with a symmetrically built molecule similar to methane itself. All these tetra-substitution products crystallise in the regular system similarly to methane. The crystal system of the substitution products of methane is thus entirely dependent upon the symmetry of the chemical molecule itself, and all the changes in the symmetry of the molecule which take place as a result of a substitution in the molecule of one univalent atom or group by another, are reproduced by a corresponding change in crystal symmetry. The conclusion may therefore be drawn that:

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 65 (1913).

> *The crystal symmetry of the simple carbon compound is a constitutive property, which is determined by the symmetry conditions of its chemical molecule.*

The remaining one-carbon-atom compounds contain the divalent atoms O or S. The atoms of these molecules lie in one plane, and it is not possible to speak of a greater or less degree of symmetry in the build of such molecules as they are in themselves of so simple a constitution. It is therefore not surprising that molecules like CO and CO_2 crystallise in the regular system. It might be expected that CS_2 should crystallise in a similar way to CO_2, but this is not the case, the CS_2 crystals possessing a low degree of symmetry. COS again stands intermediate between CO_2 and CS_2 with regard to its crystal symmetry. $COCl_2$, however, is not intermediate between CO_2 and CCl_4, as these are both regular while $COCl_2$ is tetragonal or hexagonal.

(b) *General Considerations regarding the Properties and the Symmetry of the Chemical Molecule.*—In the above discussion of the relationship between the molecular symmetry and the crystal symmetry of the one-carbon-atom compounds, the chemical molecules have been dealt with as structures capable of possessing a definite degree of symmetry.* This does of course not imply that the atoms are thought to occupy an absolutely fixed position in a kind of rigid structure forming the molecule. In order to be able to assign to a molecule a definite degree of symmetry, it is sufficient to assume, firstly, that the atoms inside the molecule are attached to the central carbon atom and drawn to this by the four valency forces of the carbon atom acting in conjunction with the valency forces of the atoms attached to it, and secondly, that the atom of each element occupies a certain definite amount of space within the molecule, which space may be styled—using a term already used in a similar sense by Barlow and Pope† and by Richards‡—the "atomic sphere of influence." In this way is produced an assemblage of atoms, or atomic spheres of influence, packed as closely to each other as possible. The questions as to how the atom itself is built up and of whether the material mass of it occupies the entire space of the sphere of influence or not, or whether the material mass is in motion or remains motionless inside the sphere of influence, are immaterial to the present discussion of the symmetry of the chemical molecule. It might, however, be pointed out briefly that, from the point of view of the corpuscular theory,§ it is not improbable that the atoms themselves remain comparatively at rest, relative to each other, inside the molecule which vibrates as a whole. We must assume that the electrons of which the atoms are built up, according to this theory, are involved in strong rotation, and that this rapid rotation of the electrons acts gyroscopically, giving stability to the position of the atoms. From such a conception of the build of the atom follows a comparatively stable mutual arrangement of the atoms inside the molecule.

There is further the question of the crystal molecules to be considered. In crystallography a distinction is often made between the chemical molecule and the "crystal-molecule," which is supposed to be composed of a great number of chemical molecules. No experimental proof exists as to the existence of such "crystal-molecules" or as to their size measured in numbers of chemical molecules. However, if such "crystal-molecules" exist, the discussion in this paper would not be in any way influenced thereby, since the "crystal-molecules" must be thought of as being small crystal units of the fully developed crystal itself, and consequently as belonging to the same crystal system as this. All that applies to the relationship between the chemical molecule and the crystal form of the compound would therefore also be applicable to the relationship between the chemical molecule and the "crystal-molecule."

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* With regard to earlier discussions on the symmetry of chemical molecules, compare Le Bel, 'Bull. Soc. Chim.' (3), vol. 3, p. 790.

† Barlow and Pope, 'Chem. Soc. Journ.,' vol. 89, p. 1675 (1906); and vol. 91, p. 1150 (1907).

‡ Richards, 'Zeitschr. Phys. Chem.,' vol. 40, pp. 169 and 597 (1902).

§ Compare J. J. Thomson, "The Structure of the Atom," 'Phil. Mag.,' 1904, p. 237. Nagaoka, 'Phil. Mag,' 1904, p. 445; J. W. Nicholson, 'Month. Not. Roy. Astro. Soc.,' vol. 72, p. 49 (1912); E. Rutherford, 'Phil. Mag.,' May, 1911, p. 669, and October, 1912, p. 461.

In the preceding discussion on the compounds containing one carbon atom the symmetry of the chemical molecule has been dealt with in a quite general way. The symmetry of a molecule may, however, be defined more precisely by adopting the definitions of symmetry which have been developed in the study of crystals.* If we now consider the carbon compounds containing only one carbon atom, which have been investigated here from the point of view of the kind of symmetry-elements by which they are characterised, we observe that methane, CCl_4, CBr_4, and CI_4, represent what we may call the tetrahedral case of symmetry, the molecule containing four three-fold and three two-fold axes of symmetry, and six planes of symmetry. A crystal of the corresponding degree of symmetry belongs to the regular system, in which the above substances accordingly have been found to crystallise. The molecule of a compound like $C(NO_2)_4$ will be characterised by the same elements of symmetry as CH_4, since the three atoms in the nitro-group must lie in a single plane, and will therefore not alter the symmetry of the molecule when introduced instead of H or the halogens. That this body CN_4O_8 crystallises in the regular system is therefore of considerable interest.

In a tetra-substitution product of the type CR_4, each of the four substituents occupies an equal amount of space, and whether the total amount of space jointly occupied by the four substituents is the same as that occupied by the four hydrogen atoms in methane or not, or whether the sphere of influence of the central carbon atom is altered on account of the mutual forces attracting the atoms to each other (the valency forces), or on account of the close packing of the atomic spheres of influence, or not, the symmetry of the molecule remains the same. But if a substituent X of different nature is introduced the question arises, whether this occupies an amount of space different from that of R (*i.e.*, a different atomic volume) or not, and whether the specific properties of the sphere of influence of X will in some respect alter the spheres of influence of the carbon atom and of the three remaining atoms R. Supposing that the substituent occupies the same amount of space, then clearly the symmetry would not be altered in any way, and in consequence we might expect to find all the simple substitution products of methane regular, as is methane itself and its tetra-substitution products of the type CR_4. This is, however, not the case, and we must therefore conclude that a substituent X introduced into the molecule will either not necessarily occupy the same amount of space as R, or that it will affect in some way the sphere of influence of the carbon atom.

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* The definition of the symmetry laws and the terminology of the symmetry elements, as given in Groth's 'Physikalische Kristallographie,' will be followed here.

If the substituent X only occupies a different amount of space, but does not alter the sphere of influence of the carbon atom, then all such substitution products, CR_3X, would possess a molecule of trigonal symmetry,* and we might expect these substitution products to crystallise in the trigonal (or hexagonal) system, and to differ from each other principally in the ratio between their principal axis and their lateral axes. If, however, the substituent affects the sphere of influence of the carbon atom, on account of the mutual attraction between these atoms, the sphere of influence of the carbon atom and probably also that of the substituent itself will be deformed, as a result of which the valency direction C—X may be altered as compared with the corresponding valency direction in the molecule CR_4. The molecule of the substitution product CR_3X will in such an event possess only one plane of symmetry but no axes of symmetry, and we may expect such a body to crystallise in the monoclinic system.

Now the experimental results show that the substitution products of methane of the type CH_3R are, as a rule, monoclinic, whereas the substitution products of the type CHR_3 are hexagonal (or trigonal). That is, when the atomic volume of the group X in CR_3X is large compared with that of R (R in this case = H) and of C, such a distortion of the direction of the valency-force C—X takes place, but when the atomic volume of the group X is small compared with that of R (R in this case = Cl, Br, I) no distortion of the valency direction C—X manifests itself in the crystalline form of the substitution products.

From the difference in crystal form of the mono-substituents examined from that of the tri-substituents, we thus arrive at the conclusion that:

> the properties (mass) of the four atomic spheres of influence connected with the carbon atom influence, to some extent, the sphere of influence of the carbon atom, whereby the symmetry of the molecule may be affected. The specific properties of the atoms connected with the carbon atom thus indirectly influence the crystal form of the body.

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* One trigonal axis of symmetry passing through C and X, and three planes of symmetry passing through this axis.

If we then turn to the di-substitution products, we again find that if the substituents X in a body CR_2X_2 occupy the same amount of space as the atoms R, and do not influence the sphere of influence of the carbon atom in a different way from R, then such a di-substitution product ought to be regular. If, however, the volumes occupied by R and by X are different, or if the effect on the atomic sphere of influence of the central carbon atom is of a different order, the molecule CR_2X_2 will show orthorhombic symmetry, and possess a two-fold axis of symmetry and two planes of symmetry which pass through the axis, but which differ one from the other. This is what actually takes place; the di-substitution products investigated have all been found to be orthorhombic.

The conclusions we arrive at as to the mutual influence of the "sphere of influence" of the different atoms upon each other are not surprising, from the point of view of the theory of the compressibility of the atoms which has been put forward by Richards,* and which has been shown by him to explain in a satisfactory way so many of the phenomena connected with the properties of the atoms.† In fact, the results given here may be regarded as forming a further proof of the value of the theory of compressible atoms as applied to the study of crystalline form, a value which has recently been pointed out by Richards in a paper on "The Chemical Significance of Crystalline Form."‡ In all the examples of bodies of the type CR_3X studied here, the difference between the atomic volume of any of the substituents and that of hydrogen is very large, all the substituents also having a larger atomic volume than the carbon atom. There are, however, at present, not sufficient experimental results available to permit of the question being answered as to whether the bulk of an atom, in itself, is sufficient to cause a deflection of the direction in which the valency force of the carbon atom acts from the direction in a regular tetrahedron, or whether the specific properties (build, shape) of the atom are the real cause of this deflection.§ Since the compressibility of the elements, as Richards has shown, is a periodic function, just as the atomic volume is, we may also expect that the influence which a substituent has on the crystal symmetry will not alone depend upon its absolute mass but may be a periodical function of the mass.

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* Th. W. Richards, 'Zeitschr. Phys. Chem.,' vol. 40, pp. 169 and 597 (1902).

† Th. W. Richards, "Faraday Lecture," 'Chem. Soc. Journ.,' vol. 99, p. 1201 (1911).

‡ Th. W. Richards, 'Amer. Chem. Soc. Journ.,' 1913, p. 381.

§ It may also be pointed out that the crystal systems are not separated from each other in any very distinct way, but that forms which show a "pseudo-symmetry" of a higher system often occur. There are forms which keep a kind of intermediate position between several other forms, and a small distortion in one or the other respect therefore in such cases is sufficient to bring about a change to either a higher or a lower degree of symmetry. The case of a trigonal pyramid is of special interest, and may therefore be quoted as an example: a slight distortion in one direction may lead either to a regular, an orthorhombic, or a monoclinic symmetry. In large molecules especially we must expect that alterations in the crystal symmetry may take place, for example, when a

(c) *Compounds containing Several Carbon Atoms.*—When the simplest carbon radical, the methyl group —CH_3 is successively introduced into the methane molecule, taking the place of the four hydrogen atoms, we obtain ethane, propane, trimethyl-methane, and tetramethyl-methane. As seen from the table on p. 2, ethane is hexagonal, propane probably rhombic, trimethyl-methane hexagonal, and tetramethyl-methane regular. The crystal symmetry of these hydrocarbons corresponds thus to the symmetry of their molecules. In this case the monosubstitution product and the trisubstitution product are both hexagonal (or trigonal). The molecule of ethane is peculiar in this respect, that the substituent is identical with the remaining nucleus of the compound into which it enters, and a molecule of this kind consequently possesses a higher degree of symmetry than any other monosubstitution product CH_3R.

In the case of longer carbon chains, a different degree of symmetry may in many instances be ascribed to the molecules, depending upon the view taken as to which part of the molecule may be regarded as a substituent, for example, propane may be regarded—as it is above—as dimethyl-methane, that is, as a di-substitution product, or as ethyl-methane $CH_3.C_2H_5$. In the first alternative the symmetry of the molecule would be orthorhombic, in the latter monoclinic. It seems that, in cases like this, it is correct to assume that the molecule really possesses the highest degree of symmetry which can be allotted to it. The symmetry of a long carbon chain will also largely depend upon the actual way in which the atoms in such a chain are close packed. Of the hydrocarbons containing such long chains, *n*-butane crystallises, similarly to ethane, in the hexagonal system; *n*-hexane and *n*-octane are, however, monoclinic or triclinic. The experimental results with regard to *n*-pentane and *n*-heptane are less definite, but, in any case, it seems certain that the normal hydrocarbons containing more than four carbon atoms all crystallise in the systems of least symmetry. It is remarkable that the two lowest members of the series containing an even number of carbon atoms should agree in their crystalline form and differ from the members containing an odd number of carbon atoms. This forms an analogy with their behaviour as regards their melting points, the lower

substituent of unsymmetrical build is introduced in the place of a symmetrically built radical, or when an atom of great atomic volume is introduced in the place of one of small atomic volume.

members of the series forming two different groups, the series with an even number of carbon atoms melting, as is well known, at a comparatively higher temperature than the series with an uneven number of carbon atoms in the molecule.

In tetramethyl-methane each of the four groups connected to the central carbon atom is in itself a body in space. As, however, the group $—CH_3$ is symmetrically built, the symmetry of the methane molecule is not diminished, but is, on the contrary, increased. That tetramethyl-methane crystallises in the regular system may therefore be regarded as an important confirmation of the theory. If one of the hydrogen atoms in each of the methyl groups were, however, substituted by some other atom or group, we might expect that the resulting product would not crystallise in the regular system, as the four groups in themselves would then no longer be of symmetrical build. We may therefore expect that tetra-ethyl-methane and tetra-propyl- or isopropyl-methane would not be regular, while tetra-tertiary-butyl-methane again would be regular. These hydrocarbons have not yet been prepared synthetically. The penta-erythrite $C(CH_2OH)_4$ can, however, be regarded as tetramethyl-methane in which one hydrogen atom in each of the methyl groups has been substituted by the $—OH$ group, thereby rendering these four groups unsymmetrical in build. As a result thereof, the molecule contains only one four-fold axis of symmetry and four planes of symmetry, instead of four three-fold axes, three two-fold axes, and six planes of symmetry. Now, penta-erythrite crystallises in the tetragonal system, which is entirely in accordance with the existence of a four-fold axis of symmetry in its molecule. With regard to the tetra-ethyl-ether of the orthocarbonic acid $C(O.CH_2CH_3)_4$, the case is very similar. The introduction of the ether-oxygen atom would probably not alter the symmetry of the molecule as compared with $C(CH_3)_4$, but the $—CH_2CH_3$ group is not of symmetrical build, and, in consequence, the molecule possesses only one four-fold axis of symmetry and four symmetry planes. In accordance therewith the ether is tetragonal, but the analogy in build of the molecule with that of tetramethyl-methane is also indicated by its pseudo-regularity. The methyl-ether of orthocarbonic acid would probably be found to crystallise in the regular system, but this body has not yet been prepared.

In the class of the alcohols, the trimethylcarbinol is of interest, as its molecule contains a three-fold axis of symmetry. In accordance herewith it crystallises in the hexagonal system. Of the ethers, the simplest, the dimethyl ether $CH_3.O.CH_3$, is rhombic. It is built very similarly to ethane, but on account of the introduction of the O-atom the atoms in the molecule cannot, probably, be close packed in as symmetrical a way as in the case of ethane, the result of which is that the ether crystallises in a system of lower symmetry than ethane. If one of the hydrogen atoms is substituted by a methyl group, we obtain the methyl-ethyl-ether in which the symmetry plane passing through the O-atom of the dimethyl-ether no longer exists. This ether is monoclinic. When a hydrogen atom in the other methyl group is then substituted by a methyl group, the two groups connected with the ether-oxygen again become similar; the substitution product, the diethyl-ether, crystallises in the orthorhombic system. The influence of the degree of symmetry of the chemical molecule on the crystal form of the substance is thus distinctly shown by the ethers also.

Amongst the unsaturated hydrocarbons, ethylene is monoclinic, but acetylene regular. The atoms in acetylene will, on account of the triple linking of the carbon atoms, probably all lie in one straight line, and it is, therefore, not surprising that this body crystallises in a symmetrical way. This is also the case with other simple compounds containing a triple linking, thus $KC\vdots N$ is regular. Acetylene-di-iodide, $CI\vdots CI$, as obtained from solutions at ordinary temperature, is rhombic; this is, however, probably a modification corresponding to the double-refracting modification of acetylene which is stable at low temperature.

Ethylene occurs only in one modification, which is monoclinic, and so are also ethylene di-iodide, $CHI{:}CHI$, and ethylene tetra-iodide, $CI_2{:}CI_2$, as obtained from solution at ordinary temperature. Ethylene and the tetra-iodide contain only substituents which are identical among themselves. The cause of the low degree of symmetry of the crystal form of these two bodies must therefore be sought in a deforming influence of the ethylene link. Further experimental evidence is, however, desirable on this special point.

Of hydroaromatic hydrocarbons, only trimethylene, hexamethylene and methyl-hexamethylene have been investigated, as the other polymethylenes are unfortunately not easily accessible, and it would mean too great a loss of time to prepare them specially for an investigation of the present kind.

In trimethylene, the three carbon atoms forming the ring must necessarily lie in one plane, and we must in consequence expect the molecule to possess one trigonal axis of symmetry and to crystallise in the trigonal system. As far as the optical investigation enables us to conclude this is also the case. Hexamethylene is regular. Of the hexa-substitution products $C_6H_6Cl_6$ and $C_6H_6Br_6$ both cis-forms and trans-forms exist. The form of the hexachloride which is described as the "cis-form" is pseudo-regular, and the form described as the "trans-form" is monoclinic. The form of the hexachloride which is here referred to as "pseudo-regular" is one of those bodies of which it is, on account of the optical anomalies it exhibits, extremely difficult to say to which of two crystal systems it really belongs. The crystals, as measured goniometrically, are regular, but the optical properties indicate that they are hexagonal. The corresponding form of the hexabromide is regular also in its optical properties. There are evidently in this case quite special circumstances —probably connected with the way the atoms in such a molecule may be close packed—which render it possible for the molecules to assume a higher degree of crystalline symmetry than the hexagonal which would correspond to the actual degree of symmetry of the molecule if we assume that the six carbon atoms all lie in one plane. If one of the hydrogen atoms in such a molecule of hexagonal symmetry is substituted the symmetry is changed to monoclinic. An example thereof is furnished by monomethylhexamethylene, which actually is monoclinic.

We then pass over to the aromatic compounds. Benzene itself is orthorhombic. Toluene is also orthorhombic, and thus substitution of a hydrogen atom by a methyl group does not affect the crystal system. A di-substitution in the para-position, however, distorts the orthorhombic symmetry of the benzene nucleus: para-xylene is monoclinic. If several methyl groups enter into a symmetrical position in the benzene molecule, the crystal symmetry is not changed; mesitylene and hexamethyl-benzene are orthorhombic.

From the composition C_6H_6, one might expect that benzene itself should be hexagonal. It is, therefore, probable that the double links, or whatever may be the peculiar disposition of the valency forces in the benzene nucleus, here, as in the case of the ethylene derivatives, are instrumental in bringing about a lower degree of symmetry of the molecule than that which it might be expected to have. As the build of the benzene nucleus itself is not altered by substitution of the hydrogen atoms, and as the phenyl group, moreover, is a group of comparatively large mass, those circumstances which affect the symmetry of benzene itself will also manifest themselves in their effect upon the symmetry of the compounds into which phenyl enters as a substituent. If we thus consider the successive substitution products of methane in which the phenyl group is the substituent, we have toluene, $CH_3.C_6H_5$, diphenylmethane, $CH_2(C_6H_5)_2$, triphenylmethane, $CH(C_6H_5)_3$, and tetraphenylmethane, $C(C_6H_5)_4$, which are all orthorhombic. In all these cases the nucleus of the parent substance is very small in comparison with the phenyl group or groups, and it is therefore of very little morphotropic influence on the symmetry of the phenyl groups, which remains dominant.

Isomorphism, Morphotropy, and Enantiomorphism from the Point of View of the Theory.

In the introduction to Part I of this paper* it was pointed out that the phenomena of isomorphism, of morphotropy, and of enantiomorphism each indicated the existence of a general relationship between the crystalline properties of a substance and its chemical constitution, although sufficient data were not previously known which might have served to establish a theory, correlating and explaining the evidence as established separately by these phenomena. If the theoretical views on the interdependence of the chemical constitution and crystal form of the simpler organic bodies arrived at in the preceding chapters are correct, they must not only enable us to give an explanation of the isomorphism of complicated bodies and of the phenomena of morphotropy and of enantiomorphism, but also of the mutual relationship between these three phenomena.

If we compare two isomorphic bodies with one another, we find that their molecules differ only in this respect, that an atom of a certain element in one is in the other replaced by an atom of a chemically related element. The general architecture of the molecule and its symmetry are not affected by such a substitution. If, however, instead of an atom of the same valency and of similar properties an atom of a different valency and of different nature altogether is introduced, then the atomic spheres of influence of the other atoms in the molecule will be sufficiently affected to cause changes of a more general kind in the symmetry conditions of the molecule, and the product will, in consequence, no longer be found to be isomorphic with the parent substance. *The phenomena of isomorphism are thus explained by the fact that elements which are able to replace each other isomorphically are sufficiently similar to cause no alteration of the symmetry of the molecule when replacing each other.* The atoms replacing each other isomorphically have, however, a different atomic volume, and we must therefore expect that the amount of space they occupy will manifest itself in the crystal dimension of the bodies. Now this is exactly what happens in isomorphic series. The exact measurements by Tutton have shown that the change in crystalline dimensions of isomorphic bodies may, even to their numerical value, be deducted from the space occupied by the atoms which replace each other isomorphically.

In an entirely analogous way the phenomena of morphotropy are explained by the theory of the interdependence of crystal symmetry and molecular symmetry. If an atom or radical in a comparatively large molecule is replaced by another atom or radical, a more or less strong deformation of the atomic spheres of influence takes place according as the new substituent is more or less similar to the original one. The substitution will manifest itself in a gradual change of the crystal form to a form more and more different from that of the original parent substance, as the substituent becomes more and more different in character or degree of symmetry from the original substituent, or as the mass of the substance becomes larger in comparison with that of the nucleus into which it enters.

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* 'Roy. Soc. Proc.,' A, vol. 88, p. 354 (1913).

These circumstances afford also the explanation of the fact that some bodies of a rather complicated constitution crystallise in the regular crystal system; they contain a comparatively large number of atoms and radicals distributed in a way which makes the molecule sufficiently symmetrical to cause it to crystallise in the regular crystal system, and the unsymmetrical groupings of atoms which may be contained in such a molecule are not of sufficient "morphotropic influence" to cause an alteration of the general symmetry of the molecule as manifested in its crystal form.

Lastly, with regard to the enantiomorphism, Pasteur was the first to prove that substances which in the liquid or dissolved state are able to rotate the plane of polarisation crystallise in enantiomorphic forms. Becke then showed that, independently of the crystal system in which a substance of this kind crystallises, such enantiomorphic forms always belong to one of those nine crystal classes which contain neither planes of symmetry nor planes of compound symmetry but only axes of symmetry.* Becke also pointed out that a chemical molecule which contains an "asymmetric carbon atom" in the sense of van't Hoff and Le Bel is devoid both of planes of symmetry and of planes of compound symmetry. The enantiomorphism of optically active substances is therefore a further consequence of the general law of the interdependence of the crystal symmetry and the molecular symmetry. In this case it is the lack of symmetry of the molecule, which is reproduced in the crystals by a corresponding lack of planes of symmetry. The law of Pasteur, therefore, from this point of view appears as a special case of a general law.

As the law of Pasteur holds good also with regard to molecules of very complicated build, of which it is not possible at present to say definitely what mutual arrangement the atoms occupy inside the molecule, we are justified in concluding that the general law of the interdependence of molecular symmetry and of crystal symmetry applies even to such complicated cases. As an example in which this is actually proved by investigation, the group of the alums, $(SO_4)_4Al_2K_2,24H_2O$ (in which K = Na, Li, Rb, Cs, NH_4; Al = Cr, Fe), may be quoted. The alums containing the alkaline metals and aluminium or chromium all crystallise in the "dyakis-dodecahedral" class of the regular crystal system. It is probably the disposition of the 24 H_2O groups which gives the molecule a sufficient degree of symmetry to crystallise in the regular system, and the mutual arrangement of the atoms in the group $Al_2K_2(SO_4)_4$ does not interfere therewith. Crystals belonging to the dyakis-dodecahedral class of the regular system are characterised by three two-fold and four three-fold axes of symmetry and by three planes of symmetry at right angles to the three two-fold axes. Ammonium alum crystallises similarly to the alkaline alums, and so does also trimethylamine alum. The active amylamine alum, however, crystallises in the "tetrahedral-pentagonal-dodecahedral" class, which is characterised by the same number of axes of symmetry, but in which no planes of symmetry occur. By the introduction into the molecule, in the place of the symmetrical CH_3 group, of the active amyl group, the general regular character of the alum molecule is thus not altered, but as the molecule can now no longer contain any planes of symmetry, this particular alum, as a consequence, crystallises in a class of the regular system devoid of symmetry planes.

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* F. Becke, 'Tschermak's Mineralog. und Petrogr. Mitteil.,' vol. 10, p. 464, and vol. 12, p. 256.

The general results to which this investigation has led thus enable us to explain the phenomena of isomorphism, as well as of morphotropy and of enantiomorphism, as all depending on one and the same fundamental relationship governing the interdependence between the molecular constitution and the crystal form of a body, and which may be summarised thus: "The symmetry of the chemical molecule of a substance determines its crystal symmetry."

General Considerations as to the Qualitative and Quantitative Side of the Theory.

The relationship between the molecular constitution and the crystal symmetry has been discussed here from the general, that is to say, qualitative, point of view and the solution of the problem arrived at is also of a qualitative kind. No common quantitative, numerical solution of this problem of course exists, but the influence of each radical or atom upon the numerical crystallographical data has to be studied separately in each case, not only from the point of view of the effect produced by the substituent on the nucleus into which it enters, but also with regard to the effect the nucleus produces on the substituent. Investigations on isomorphic and morphotropic series furnish the numerical data in each special case.

The mutual relation between the qualitative and quantitative interdependence of molecular constitution and crystal-form is, in a way, similar to what is the case regarding the optical rotatory power of organic compounds. The theory of the "asymmetric carbon atom" solved this problem quite generally in a qualitative sense, but the determination of the actual numerical influence of each atom, or group, on the total rotation of the compound meets with great difficulties.

Extension of the Theory to Compounds other than Carbon Compounds.

The existing data concerning other tetravalent elements indicate that the theory developed here for the interdependence of molecular and crystal symmetry of the simpler organic compounds may be extended to other compounds, in a similar way as the theory of the asymmetric carbon atom. Thus the following compounds of the general type AR_4 are regular: SiI_4, TiI_4, SnI_4, $IrCl_4$, UCl_4; and the following compounds of the type AX_2R_2 are orthorhombic: $Sn(CH_3)_2Cl_2$, $Sn(C_2H_5)_2Cl_2$, $Sn(C_3H_7)_2Cl_2$, $Sn(CH_3)_2(CHO_2)_2$. No data are available at present concerning compounds of the types AXR_3 and AX_3R. Further investigations are therefore necessary, and the author intends to extend this research to Si, Ti, Sn, Pb, and other compounds. However, the cases mentioned above make it already now almost certain that the relation expressed by the theory is not limited to carbon compounds.

The Relationship between the Chemical Constitution and the Occurrence of Polymorphic Modifications.

With regard to the relationship between the chemical constitution and the occurrence of polymorphic modifications, the following may be said already at this stage of the investigation: Vorländer has shown, as a result of his elaborate investigations on the occurrence among organic bodies of liquocrystalline modifications, that the existence of such modifications is intimately connected with the occurrence of long carbon chains, and with the occurrence of para-substituents in the benzene nucleus. As the liquocrystalline modifications must be regarded as a kind of polymorphic modifications, it seems not improbable that the occurrence of polymorphism is actually a constitutive property. The existence of polymorphic modifications of nearly all the simplest substitution products of methane confirms this view. It further suggests that methane itself also might be polymorphic. Methane was therefore investigated at liquid hydrogen temperatures, and it was found that an enantiotropic transition into a double-refracting modification really takes place at a very low temperature, quite analogously to what is the case with respect to the other carbon compounds of the type

CR_4.—It has, further, been noticed that the position of the transition point in the substitution products of methane relative to their melting point is influenced in a regular manner by the nature of the substituent. The transition points situated at low temperature have, however, so far been determined only quite approximately, and a more detailed discussion of this question must, therefore, be postponed until more accurate temperature determinations have been made.

Before concluding this paper, I have to acknowledge the liberality with which the technical resources of the Davy-Faraday Laboratory, in which the investigation was carried out during the year 1912 and the earlier part of 1913, have been placed at my disposal. I wish also to thank Sir James Dewar for the interest he has shown in this work, whereby he has greatly furthered its progress.

On a Meteoric Iron from Winburg, Orange Free State.

By W. A. Douglas Rudge, M.A.

(Communicated by Prof. B. Hopkinson, F.R.S. Received October 10, 1913,—
Read February 26, 1914.)

(Plates 1 and 2.)

Some account of this meteorite has been given in the 'Transactions of the Royal Society of South Africa,' 1912, vol. 2. The present communication deals more fully with the internal structure of the meteorite, giving also some account of the mechanical and magnetic properties.

The meteorite was seen to fall in 1881 by some natives working on the Zeekoegat farm, belonging to Dr. Schneehage. They reported the matter to their employer, who ordered them to carry the meteorite to the farmyard, where it remained some years, finally being sent to the Bloemfontein Museum. The meteorite measured 38 by 23 cm. along the two greatest axes and weighed nearly 50 kgrm. It was slightly magnetic, having a number of poles. It will be convenient to divide this paper into sections, viz.:—

(1) Dealing with the chemical composition.
(2) ,, ,, internal structure.
(3) ,, ,, mechanical properties.
(4) ,, ,, magnetic properties.